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(71)Applicant: NIKON CORP

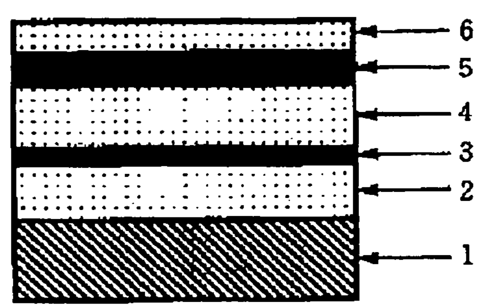
(72)Inventor: MATSUURA KEIJI

(54) REFLECTION PREVENTIVE FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a high reflection preventive effect in a wide band over a prescribed wavelength range, and provide a high reflection preventive effect for a wide incident angle by forming a low refractive index layer in first, third and fifth layers by counting from the base board side on a base board to pass the light having a specifice wavelength, forming a high refractive index layer in second and fourth layers, and specifying their optical film thicknesses.

SOLUTION: A low refractive index layer is formed in first, third and fifth layers 2, 4 and 6 by counting from the base board 1 side on a base board 1 to pass the light having this wavelength at least to an optical design reference wave length λ_0 in a wave length range of a wavelength of 180 to 300nm, and a high refractive index layer is formed in second and fourth layers 3 and 5, and a reflection preventive film is formed. An optical film thickness of the first and the third layers 2 and 4 is set in a range of about $0.5\lambda_0$ to $0.7\lambda_0$, and an optical film thickness of the second layer 3 is set in a range of 0 to about $0.15\lambda_0$, and an optical film thickness of the fourth and the fifth layers 5 and 6 is set to about $0.5\lambda_0$ to $0.3\lambda_0$. The optical film thickness of the first layer 2 and the optical film thickness of the third layer 4 are set in the almost same film thickness.



CLAIMS

[Claim(s)]
[Claim 1] On the substrate which penetrates the light of the aforementioned wavelength at least to the arbitrary design-basis wavelength lambda 0 of with a wavelength of 180-300nm wavelength within the limits Count from a substrate side and a low refractive-index layer is formed in the 1st layer, the 3rd layer, and the 5th layer. It is the antireflection film which comes to form a high refractive-index layer in the 2nd layer and the 4th layer. the optical thickness of the 1st layer and the 3rd layer -- about 0.5lambda0- within the limits of about 0.7lambda0 -- it is -- the optical thickness of the 2nd layer -- 0- the antireflection film characterized by being within the limits of about 0.15lambda0, and the optical thickness of the 4th layer and the 5th layer being about 0.15lambda0 to 0.3lambda0
[Claim 2] The antireflection film according to claim 1 characterized by the optical thickness of the 1st aforementioned layer and the optical thickness of the 3rd aforementioned layer being abbreviation same thicknesss.
[Claim 3] The antireflection film according to claim 1 or 2 characterized by the refractive index of the aforementioned low refractive-index layer, the refractive index of the aforementioned quantity refractive-index layer, and the refractive index of the aforementioned substrate satisfying the relation of nL<=nS<=nH. However, for the refractive index of a low refractive-index layer, and nS, the refractive index of a substrate and nH are [nL] the refractive index [a claim 4] of a high refractive-index layer. The material of the aforementioned low refractive-index layer Lithium fluoride (LiF), barium fluoride (BaF2) Strontium fluoride (SrF2), aluminum fluoride (AlF3), Magnesium fluoride (MgF2), a calcium fluoride (CaF2), A sodium fluoride (NaF), a ******** light (Na3AlF6), They are one or more components chosen out of the group of a thio light (Na5aluminum3F14), silicon dioxides (SiO2) and such quality of mixture, or a compound. The material of the aforementioned quantity refractive-index layer Fluoride lanthanum (LaF3), gadolinium fluoride (GdF3) Neodium fluoride (NdF3), a fluoride dysprosium (DyF3), Yttrium fluoride (YF3) and thorium fluoride (ThF4), an aluminum oxide (aluminum2O3), The multilayer antireflection film according to claim 1 to 3 characterized by being one or more components chosen out of the group of magnesium-oxide (MgO) and lead fluoride (PbF2), such quality of mixture, or a compound.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to an antireflection film which shows a very low reflection factor to a ultraviolet radiation.
[0002]
[Description of the Prior Art] In order to increase the degree of integration of a semiconductor device in recent years, the demand of a raise in the resolution of the reduction projection aligner (stepper) for a semiconductor manufacture is increasing. Short wavelength-ization of light source wavelength is mentioned as the one technique of raising the resolution of the photo lithography by this stepper. Recently, utilization of the stepper who could oscillate the light of a short wavelength region from the mercury lamp, and used the high power excimer laser as the light source has started. In this stepper's optical system, in order to reduce a quantity of light loss, a flare ghost, etc. by surface reflex of optical elements, such as a lens, it is necessary to form an antireflection film. Moreover, although there are KrF excimer laser (lambda= 248.4nm), an ArF excimer laser (lambda= 193.4nm), etc. as excimer laser which is the light source, when the large layer matter of absorption and the low layer matter of laser-proof nature constitute an optical thin film to such light, it becomes easy to cause substrate side change, a layer breakdown, etc. by a quantity of light loss and absorption generation of heat by absorption. For this reason, what has low absorption and laser-proof [quantity] nature as layer matter to use is desirable. The modality is restricted although the layer matter which can be used on the aforementioned excimer laser wavelength is a fluorine compound mainly like magnesium fluoride (MgF2), and a part of oxide. Moreover, the substrate used similarly is also restricted to fluorine compound crystals, quartz glass, etc., such as fluorite.
[0003] the example of the conventional antireflection film ****** -- drawing 14 -- the thing of a configuration [like] is known This serves as the two-layer configuration to which the laminating of the high refractive-index layer 12 and the low refractive-index layer 13 was carried out one by one on the substrate 11. When the acid-resisting conditions in the antireflection film of a two-layer configuration set [the refractive index of a substrate / the refractive index of ns and a medium] the refractive index of nL and a high refractive-index layer to nH for the refractive index of n0 and a low refractive-index layer, it is known that it is ns/n 0<=(nH/nL) 2. In design center wavelength lambda0=193.4nm, when a fluoride lanthanum (LaF3, n= 1.69) and the low refractive-index layer 13 are made into magnesium fluoride (MgF2, n= 1.42) for quartz glass (n= 1.56) and the high refractive-index layer 12 and a substrate 11 is applied to the aforementioned acid-resisting conditions, it is set to 1.56 / 1> (1.69/1.42) 2**1.42, and it turns out that acid-resisting conditions are not fulfilled. in lambda= 193.4nm, a reflection factor becomes the lowest by the conventional two-layer antireflection film which used the above substrates and the layer matter -- substrate The 1st layer of quartz glass LaF3 0.25lambda0 -- the 2nd layer MgF2 It is in the case of the thickness configuration of 0.25lambda0Air.
[0004] The optical admittance view in lambda0=193.4nm is shown in the reflective property and the drawing 16 in the incident angle of theta= 0 degree in drawing 15 at the degree property of incident angle and the drawing 17 in lambda0=193.4nm. The conventional two-layer antireflection film understands that residual reflex is about 0.2% in lambda0=193.4nm from the reflective property of drawing 15 . When this conventional two-layer antireflection film is used for the optical system which consists of 50 lenses, light can penetrate the two-layer antireflection film of the 100th page, and about 20 about% (1-(1-0.002)100=0.18) of the quantity of light cannot be penetrated by this residual reflex, but it will lead to a fall of exposure luminous efficacy.
[0005] Furthermore, a flare ghost's etc. cause will cause a fall of exposure precision. It is necessary to bring close to the point (1, 0) which shows the refractive index of a medium, i.e., air, for the terminal point of the tracing of admittance in the optical admittance view of drawing 17 for reducing such residual reflex. It can consider using the low refractive-index matter of a refractive index lower than the high refractive-index matter of the refractive index higher than the substrate of a lower refractive index as matter which fulfills the aforementioned acid-resisting conditions for that purpose. However, since the modality of the substrate which can be used, and layer matter was restricted as mentioned above, with the conventional two-layer configuration, some residual reflex was what is not avoided.
[0006] The antireflection film which solves such a problem is indicated by JP,61-77001,A. The antireflection film indicated by JP,61-77001,A consists of five layer structures of 1.5 or less low refractive-index layer and the interval refractive-index layer of 1.6-1.8, the sums of the optical thickness of the 1st layer to the 3rd layer are abbreviation lambda0/2 from a substrate side, and the optical thicknesss of the 4th layer and the 5th layer are lambda0/4.
[0007]
[Problem(s) to be Solved by the Invention] However, since the lens used with optical system has curvature, as for the antireflection film formed in the front face, thicknesss differ in the core and the circumference section. Generally, both, it applies to the circumference section from the core, a thickness becomes thin gradually, and the lens with smaller radius

of curvature of a convex lens and a concave lens of this inclination is more remarkable. For this reason, the acid-resisting band in the lens circumference section shifts to a short wavelength side only the part to which the thickness became small from the acid-resisting band in a lens core. Therefore, there is a problem that the effective acid-resisting band in the lens circumference section will separate from an operating wavelength field if the ratio of the thickness of the circumference section to the thickness of a core becomes smaller than a certain constant value.
[0008] That is, the conventional antireflection film has the trouble where an acid-resisting band is narrow, and the acid-resisting band made to 0.5% or less of especially reflection factors is narrow, therefore it can use only for the lens with comparatively big radius of curvature which the ratio of the thickness of a lens core and the thickness of the circumference section can form or more to 0.8 effectively. this invention aims at offering the antireflection film which is made in view of such a conventional trouble, has the high acid-resisting effect by the wide band in the arbitrary wavelength domains of lambda0=180-300nm, has especially the acid-resisting effect at a wide band that a long wavelength side is higher than design center wavelength, and has the high acid-resisting effect to the large degree of incident angle.
[0009]
[Means for Solving the Problem] this invention -- the first -- "-- on the substrate which penetrates the light of the aforementioned wavelength at least to the arbitrary design-basis wavelength lambda 0 of with a wavelength of 180-300nm wavelength within the limits Count from a substrate side and a low refractive-index layer is formed in the 1st layer, the 3rd layer, and the 5th layer. It is the antireflection film which comes to form a high refractive-index layer in the 2nd layer and the 4th layer. The optical thickness of the 1st layer and the 3rd layer is within the limits of about 0.5lambda0 - the abbreviation 0.7lambda0. The optical thickness of the 2nd layer is within the limits of 0 - the abbreviation 0.15lambda0, and the antireflection film (claim 1) characterized by the optical thickness of the 4th layer and the 5th layer being about 0.5lambda0 to 0.3lambda0" is offered.
[0010] Moreover, this invention provides the second with "the antireflection film (claim 2) according to claim 1 characterized by the optical thickness of the 1st aforementioned layer and the optical thickness of the 3rd aforementioned layer being abbreviation same thicknesss." Moreover, this invention is an antireflection film according to claim 1 or 2 characterized by the refractive index of the "aforementioned low refractive-index layer, the refractive index of the aforementioned quantity refractive-index layer, and the refractive index of the aforementioned substrate being satisfied of the relation of nL<=nS<=nH with the third. however, nL -- the refractive index of a low refractive-index layer, and nS -- the refractive index of a substrate, and nH -- the refractive index (claim 3) of a high refractive-index layer -- " is offered
[0011] The material of the "aforementioned low refractive-index layer this invention to the fourth Moreover, lithium fluoride (LiF), Barium fluoride (BaF2), strontium fluoride (SrF2) Aluminum fluoride (AlF3), magnesium fluoride (MgF2) A calcium fluoride (CaF2), a sodium fluoride (NaF), a ******** light (Na3AlF6), They are one or more components chosen out of the group of a thio light (Na5aluminum3F14), silicon dioxides (SiO2) and such quality of mixture, or a compound. The material of the aforementioned quantity refractive-index layer Fluoride lanthanum (LaF3), gadolinium fluoride (GdF3) Neodium fluoride (NdF3), a fluoride dysprosium (DyF3), Yttrium fluoride (YF3) and thorium fluoride (ThF4), an aluminum oxide (aluminum2O3), The multilayer antireflection film (claim 4) according to claim 1 to 3 characterized by being one or more components chosen out of the group of magnesium-oxide (MgO) and lead fluoride (PbF2), such quality of mixture, or a compound" is offered.
[0012]
[Operation gestalt of invention] Hereafter, the antireflection film as operation gestalt of this invention is explained, referring to a drawing. The antireflection film of the operation gestalt 1 is shown in drawing 1 . A substrate and an optical thickness the antireflection film of the operation gestalt 1 between the conventional two-layer antireflection films (only henceforth the conventional two-layer antireflection film) which the high refractive-index layer 5 and optical thickness of lambda0/4 become from the low refractive-index layer 6 of lambda0/4 Optical thicknesss are five layer structures which inserted the three-tiered structure [layer / high refractive-index / 3 / of abbreviation lambda0/10] (only henceforth a three-tiered structure) to which for the low refractive-index layer 2 of abbreviation lambda0/2 and an optical thickness to carry out, and an optical thickness comes to carry out the laminating of the low refractive-index layer 4 of abbreviation lambda0/2 one by one.
[0013] Drawing 2 is an optical admittance view in three wavelength (160nm, 193.4nm, 230nm) of the conventional two-layer antireflection film, and drawing 3 is an optical admittance view in three wavelength (160nm, 193.4nm, 230nm) of the operation gestalt 1. It turns out that the three-tiered structure inserted between the substrate and the conventional two-layer antireflection film from such a difference between drawing 2 and the drawing 3 is raising the acid-resisting effect. It is so remarkable that especially the effect separates from design center wavelength.
[0014] Synthetic quartz glass, fluorite, etc. are mentioned as a substrate 1. What has the low refractive-index layers 2, 4, and 6 lower than the refractive index of the substrate 1 used is pointed out. here Magnesium fluoride (MgF2), aluminum fluoride (AlF3), A sodium fluoride (NaF), lithium fluoride (LiF), a calcium fluoride (CaF2), Barium fluoride (BaF2) and strontium fluoride (SrF2), a ****** light (Na3AlF6), a thio light (Na5aluminum3F14), silicon dioxides (SiO2), or such quality of mixture can be used.
[0015] Even if the low refractive-index matter which is different even if it uses the low refractive-index matter respectively of the same kind is used for the low refractive-index layer 2, the low refractive-index layer 4, and the low refractive-index layer 6, they can acquire the desired acid-resisting effect. What has the high refractive-index layers 3 and 5 higher than the refractive index of the substrate 1 used is pointed out. moreover, here Neodium fluoride (NdF3), fluoride lanthanum (LaF3), gadolinium fluoride (GdF3) Fluoride dysprosium (DyF3), aluminum-oxide (aluminum2O3), and lead fluoride (PbF2) and yttrium fluoride (YF3) and thorium fluoride (ThF4), magnesium oxides (MgO), or such

quality of mixture can be used.
[0016] Even if the high refractive-index matter which is different even if it uses the high refractive-index matter respectively of the same kind is used for the high refractive-index layer 3 and the high refractive-index layer 5, they can acquire the desired acid-resisting effect. These layers are formed on a substrate 1 by the well-known vacuum deposition method, the sputtering method, the ion-plating method, etc. Hereafter, although an example explains this invention more concretely, this invention is not limited to this.
[0017]
[Example] Drawing 1 is an outline cross section of the antireflection film of an example 1 to the example 5.
The configuration of the antireflection film of the [example 1] example 1 is a configuration which is shown in Table 1.
[0018]
[Table 1]

（実施例１の膜構成）
（λ_0＝193.4nm）

物質	光学的膜厚	屈折率
Air		1.00
MgF_2	0.25 λ_0	1.42
LaF_3	0.26 λ_0	1.69
MgF_2	0.57 λ_0	1.42
LaF_3	0.08 λ_0	1.69
MgF_2	0.55 λ_0	1.42
基板	CaF_2	1.50

[0019] Drawing 4 is a spectral-reflectance property view of the antireflection film of an example 1. From the spectral-reflectance property view of drawing 4 , in the wavelength domain of about 168 to about 235nm, 0.5% or less of reflection factors can be attained, and lambda0=193.4nm which is especially design center wavelength shows that a reflection factor is 0.5% or less in about 41nm large reflexogenic-zone region by the side of long wavelength.
[0020] Drawing 5 is the degree property view of incident angle in lambda0=193.4nm of the antireflection film of an example 1. The degree property view of incident angle of drawing 5 shows that a reflection factor is 0.5% or less in the large domain whose incident angle is 0 degree - about 44 degrees.
The configuration of the antireflection film of the [example 2] example 2 is a configuration which is shown in Table 2.
[0021]
[Table 2]

（実施例２の膜構成）
（λ_0＝193.4nm）

物質	光学的膜厚	屈折率
Air		1.00
MgF_2	0.24 λ_0	1.42
LaF_3	0.26 λ_0	1.69
MgF_2	0.54 λ_0	1.42
LaF_3	0.09 λ_0	1.69
MgF_2	0.56 λ_0	1.42
基板	合成石英	1.56

[0022] Drawing 6 is a spectral-reflectance property view of the antireflection film of an example 2. From the spectral-reflectance property view of drawing 6 , in the wavelength domain of about 160 to about 232nm, 0.5% or less of reflection factors can be attained, and lambda0=193.4nm which is especially design center wavelength shows that it is 0.5% or less of reflection factors in about 38nm large reflexogenic-zone region by the side of long wavelength.
[0023] Drawing 7 is the degree property view of incident angle in lambda0=193.4nm of the antireflection film of an example 2. The degree property view of incident angle of drawing 7 shows that a reflection factor is 0.5% or less in the large domain whose incident angle is 0 degree - about 45 degrees.
The configuration of the antireflection film of the [example 3] example 3 is a configuration which is shown in Table 3.
[0024]
[Table 3]

（実施例３の膜構成）

（λ_0＝193.4nm）

物質	光学的膜厚	屈折率
Air		1.00
Na_3AlF_6	0.24 λ_0	1.38
LaF_3	0.24 λ_0	1.69
Na_3AlF_6	0.57 λ_0	1.38
LaF_3	0.11 λ_0	1.69
Na_3AlF_6	0.54 λ_0	1.38
基板	合成石英	1.56

[0025] Drawing 8 is a spectral-reflectance property view of the antireflection film of an example 3. From the spectral-reflectance property view of drawing 8 , in the wavelength domain of about 170 to about 230nm, 0.5% or less of reflection factors can be attained, and lambda0=193.4nm which is especially design center wavelength shows that it is 0.5% or less of reflection factors in about 36nm large reflexogenic-zone region by the side of long wavelength.
[0026] Drawing 9 is the degree property view of incident angle in lambda0=193.4nm of the antireflection film of an example 3. The degree property view of incident angle of drawing 9 shows that a reflection factor is 0.5% or less in the large domain whose incident angle is 0 degree - about 49 degrees.
The configuration of the antireflection film of the [example 4] example 4 is a configuration which is shown in Table 4.
[0027]
[Table 4]

（実施例４の膜構成）

（λ0＝193.4nm）

物質	光学的膜厚	屈折率
Air		1.00
Na_3AlF_6	0.28λ0	1.38
Al_2O_3	0.16λ0	1.76
Na_3AlF_6	0.62λ0	1.38
Al_2O_3	0.09λ0	1.76
Na_3AlF_6	0.56λ0	1.38
基板	合成石英	1.56

[0028] Drawing 10 is a spectral-reflectance property view of the antireflection film of an example 4. From the spectral-reflectance property view of drawing 10 , in the wavelength domain of about 170 to about 232nm, 0.5% or less of reflection factors can be attained, and lambda0=193.4nm which is especially design center wavelength shows that it is 0.5% or less of reflection factors in about 38nm large reflexogenic-zone region by the side of long wavelength.
[0029] Drawing 11 is the degree property view of incident angle in lambda0=193.4nm of the antireflection film of an example 4. The degree property view of incident angle of drawing 11 shows that a reflection factor is 0.5% or less in the large domain whose incident angle is 0 degree - about 45 degrees.
The configuration of the antireflection film of the [example 5] example 5 is a configuration which is shown in Table 5.
[0030]
[Table 5]

（実施例５の膜構成）
（$\lambda 0$＝250nm）

物質	光学的膜厚	屈折率
Air		1.00
MgF_2	$0.26\lambda 0$	1.41
LaF_3	$0.24\lambda 0$	1.64
MgF_2	$0.56\lambda 0$	1.41
LaF_3	$0.07\lambda 0$	1.64
MgF_2	$0.54\lambda 0$	1.41
基板	合成石英	1.51

[0031] Drawing 12 is a spectral-reflectance property view of the antireflection film of an example 5. From the spectral-reflectance property view of drawing 12 , in the wavelength domain of about 230 to about 303nm, 0.5% or less of reflection factors can be attained, and lambda0=250nm which is especially design center wavelength shows that it is 0.5% or less of reflection factors in about 53nm large reflexogenic-zone region by the side of long wavelength.
[0032] Drawing 13 is the degree property view of incident angle in lambda0=250nm of the antireflection film of an example 5. Although the domain of the degree property view of incident angle of drawing 13 to a reflection factor of 0.5% or less of an incident angle is 0 degree - about 23 degrees, there is reflection factor change gently and it turns out that a reflection factor is 0.7% or less in the large domain whose incident angle is 0 degree - about 46 degrees.
[0033]
[Effect of the Invention] It is the domain of 60nm or more to which such an antireflection film contains the arbitrary design center wavelength of wavelength within the limits of 180nm - 300nm in this invention, and, moreover, a reflection factor can be stopped from design center wavelength to 0.5% or less in about 36 to about 53nm large reflexogenic-zone region by the side of long wavelength as explained above.
[0034] Moreover, to the arbitrary design center wavelength of wavelength within the limits of 180nm - 300nm, the degree property of incident angle is good, and can correspond to various incident angles. Therefore, even if it applies to a lens with comparatively small radius of curvature with which the ratio of the thickness of a lens core and the thickness of the circumference section becomes smaller than 0.8, sufficient acid-resisting effect can be acquired.

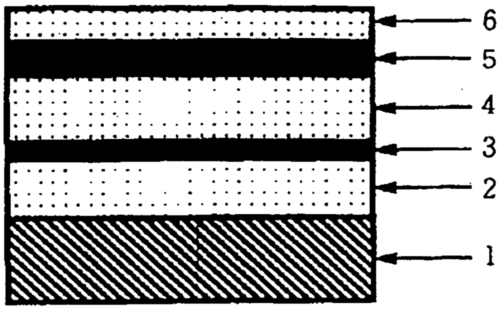
[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the outline cross section of such an antireflection film at this invention.
[Drawing 2] It is an optical admittance view in three wavelength (160nm, 193.4nm, 230nm) of the conventional two-layer antireflection film.
[Drawing 3] It is an optical admittance view [in three wavelength (160nm, 193.4nm, 230nm) of such an antireflection film to this invention].
[Drawing 4] It is the spectral-reflectance property view of the antireflection film of an example 1.
[Drawing 5] It is the degree property view of incident angle in lambda0=193.4nm of an example 1.
[Drawing 6] It is the spectral-reflectance property view of the antireflection film of an example 2.
[Drawing 7] It is the degree property view of incident angle in lambda0=193.4nm of an example 2.
[Drawing 8] It is the spectral-reflectance property view of the antireflection film of an example 3.
[Drawing 9] It is the degree property view of incident angle in lambda0=193.4nm of an example 3.
[Drawing 10] It is the spectral-reflectance property view of the antireflection film of an example 4.
[Drawing 11] It is the degree property view of incident angle in lambda0=193.4nm of an example 4.
[Drawing 12] It is the spectral-reflectance property view of the antireflection film of an example 5.
[Drawing 13] It is the degree property view of incident angle in lambda0=250nm of an example 5.
[Drawing 14] It is the cross section of the antireflection film of the two-layer configuration as a conventional example.
[Drawing 15] It is a reflective property view in the incident angle of theta= 0 degree of the antireflection film of the two-layer configuration as a conventional example.
[Drawing 16] It is the degree property view of incident angle in lambda0=193.4nm of the antireflection film of the two-layer configuration as a conventional example.
[Drawing 17] It is an optical admittance view in lambda0=193.4nm of the antireflection film of the two-layer configuration as a conventional example.
[Description of Notations]
1, 11 ... Substrate
2, 4, 6, 13 ... Low refractive-index layer
3, 5, 12 ... Quantity refractive-index layer

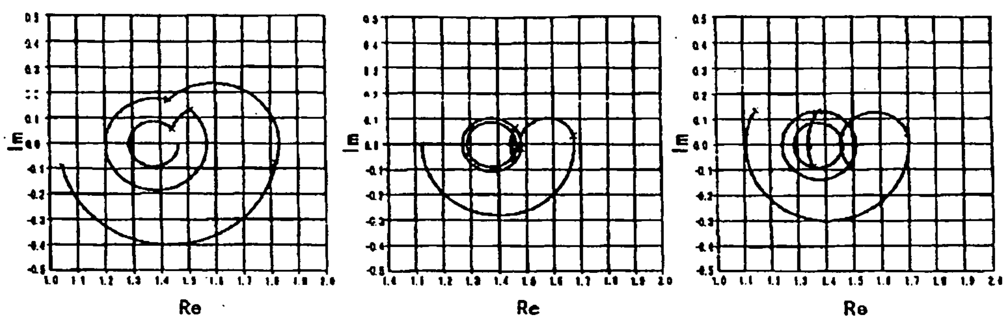
[Translation done.]

Drawing selection Drawing 1



[Translation done.]

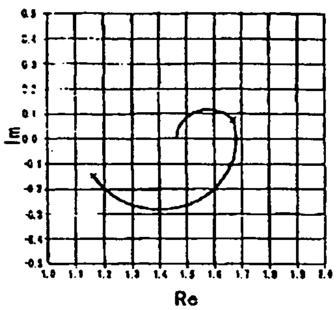
Drawing selection Drawing 2



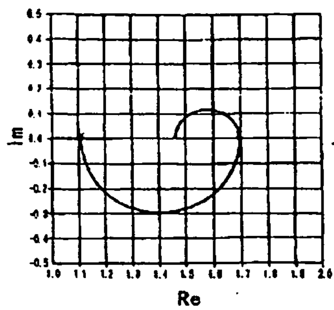
λo =160nm λo =193.4nm λo =230nm

[Translation done.]

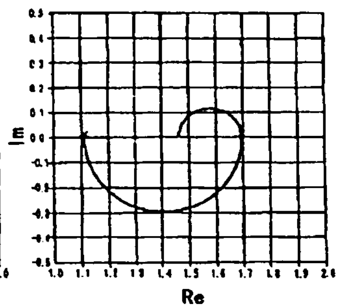
'Drawing' selection Drawing 3



λo =160nm



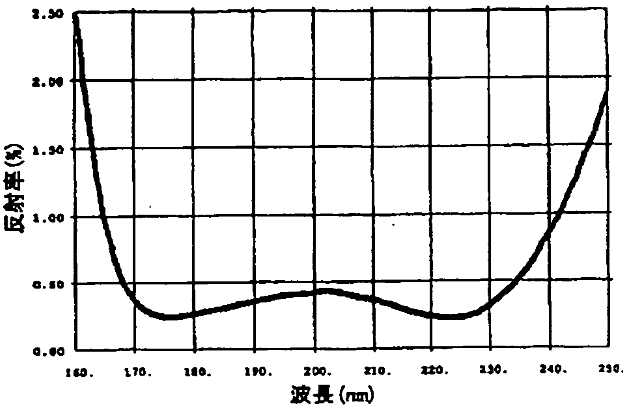
λo =193. 4nm



λo =230nm

[Translation done.]

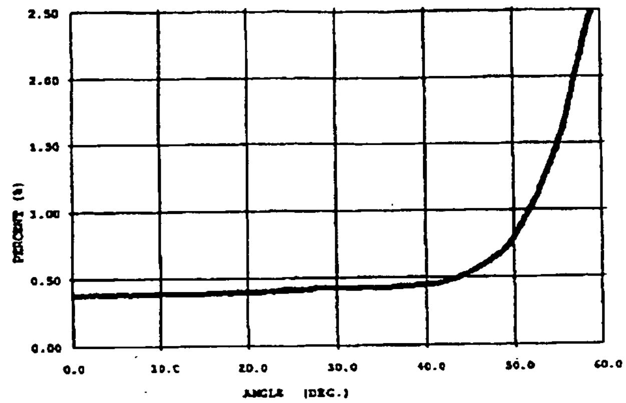
Drawing selection Drawing 4



実施例1の分光反射率特性

[Translation done.]

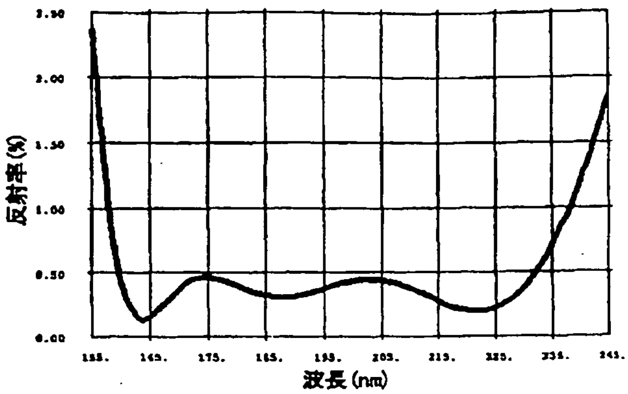
Drawing selection Drawing 5



実施例1の角度特性(at λ=183.4nm)

[Translation done.]

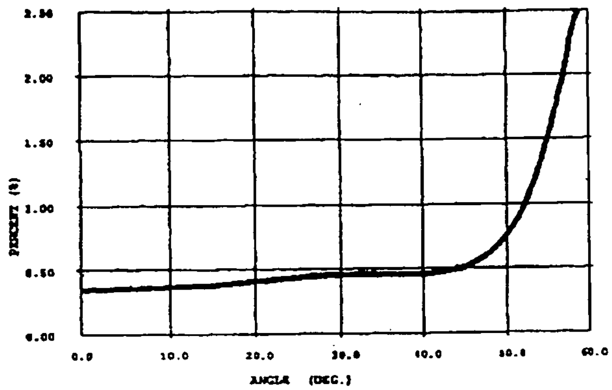
Drawing selection Drawing 6



実施例2の分光反射率特性

[Translation done.]

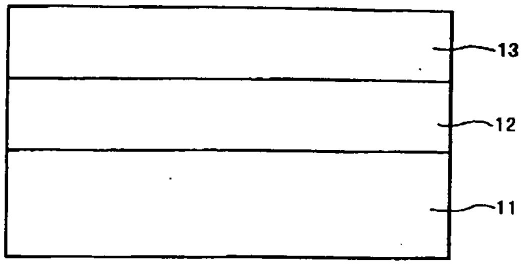
Drawing selection Drawing 7



実施例2の角度特性(at λ=193.4nm)

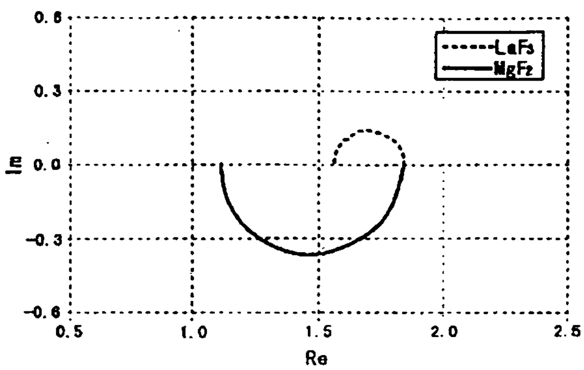
[Translation done.]

Drawing selection Drawing 14



[Translation done.]

Drawing selection Drawing 17



[Translation done.]